OCTANE RATING RELATIONSHIPS OF ALIPHATIC, ALICYCLIC, MONONUCLEAR AROMATIC HYDROCARBONS, ALCOHOLS, ETHERS, AND KETONES.*

By Gustav Egloff and P. M. Van Arsdell.

The modern internal-combustion engine owes the general smoothness of its performance to the quality of motor fuels used. There are many organic compounds which have boiling points within gasoline range which will run an automobile engine. The fuels operating to-day's engines are hydrocarbons derived from petroleum and natural gas. These gasolines have varying efficiencies that are expressed as octane ratings. The detonation properties of motor fuels are due to the type of organic molecules present, and their octane rating is a function of the structure and of the oxidation characteristics under high-temperature and pressure conditions. It should be pointed out that variation in engine conditions markedly alters the octane ratings of organic substances. Studies of the octane ratings, oxidation characteristics, and thermal stabilities of alkanes, alkenes, alkynes, cyclanes, cyclenes, mononuclear aromatics, alcohols, ethers, and ketones have been made in order to correlate the octane ratings of these compounds. Since modern synthetic processes have made individual hydrocarbons available in large volumes, their chemical structures have become increasingly important from a motor-fuel standpoint.

The relation of chemical structure to motor-fuel efficiency was first brought out in 1931, when Lovell, Campbell, and Boyd [1] published their work on the combustion properties of aliphatic hydrocarbons. These properties were reported as "aniline equivalents." In 1932 the octane-rating scale was officially established, following the work of Edgar [2] on synthesis of "*iso*-octane" and evaluation of mixtures of "*iso*-octane" in *n*-heptane.

The octane ratings of many pure hydrocarbons, alcohols, ethers, and ketones have been determined. The most extensive study so far attempted has been the work of the American Petroleum Institute, now starting the third year of its work in synthesis and determination of fuel qualities of pure hydrocarbons [3] boiling in the gasoline range. There are a number of pure hydrocarbons, alcohols, ethers, and ketones that have a higher anti-knock value than *iso*-octane and could not be rated directly on the octane scale; hence they were extrapolated.

The research, motor, and four other proposed test methods for evaluating octane numbers of gasoline are shown in Table I.

Other factors, not mentioned in test-method specifications on which octane ratings are dependent, are valve and spark timing, manifold distri-

* Paper received 14th January, 1941.

TABLE I.

*Comparison of Operating Conditions for the Gasoline Knock Test Methods using the C.F.R. Engine as a Basis.**

All methods use 3½-in. × 4½-in. variable compression cylinder, unless otherwise noted.

	Motor Method.	L-3 Method.	1939 Research Method.	Old Research Method.	C.F.R. Aviation Method (1940) (1-C).	Army Method (AN 9525) § (official for military service until Jan. 1941).
Speed.	Constant, 900 ± 9 r.p.m.	Constant, 900 ± 9 r.p.m.	Constant, 600 ± 6 r.p.m.	Constant, 600 ± 6 r.p.m.	Constant, 1200 ± 12 r.p.m.	Constant, 1200 ± 20 r.p.m.
Jacket temperature.	Constant, ± 1° F. Held between 209° and 215° F.	Constant, ± 1° F. Held between 209° and 215° F.	Constant, ± 1° F. Held between 209° and 215° F.	Constant, ± 1° F. Held between 209° and 215° F.	Constant at 374° ± 2° F. within ± 9° F.	Constant at 330° ± 2° F. within ± 5° F.
Spark advance.	Automatic, 26·0° at 5 : 1 compression ratio.	Automatic, 16° at 5 : 1 compression ratio.	Fixed, 13·0° for all compression ratios.	Automatic, 22·5° at 5 : 1 compression ratio.	Fixed, 35° for all compression ratios.	Fixed, 30° for all compression ratios.
Mixture temperature.	300° F. ± 2° F.	260° F. ± 2° F.	125° F. ± 2° F.†	Room temperature.†	Intake air 125° F. ± 5° F. Mixture temperature 220° F. ± 2° F.	Room temperature.†
Intake valve.	Shrouded.	Shrouded.	Shrouded.	Plain.	Plain.	Plain.
Fuel blends for checking engine.	49·1% C.P. benzene in A-6 equals 64·2% C-11 in A-6 (65 Oct. No.).	46·7% C.P. benzene in A-6 equals 63·5% C-11 in A-6 (65 Oct. (No.).	48·4% C.P. benzene in A-6 equals 72·5% C-11 in A-6 (70·0 Oct. No.).	65 Oct. No.	85% S-1 in M-2 vs. C.P. benzene to give same thermal plug reading.	88% *iso*-octane in *n*-heptane vs. C.P. benzene to give same thermal plug temperature.
Compression ratio for checking engine.‡	5·3 : 1.	5·5 : 1.	5·75 : 1.	5·3 : 1.	—	—
Instrumentation for determining knock.	Bouncing-pin and knockmeter.	Bouncing-pin and knockmeter.	Bouncing-pin and knockmeter.	Bouncing-pin and knockmeter.	Thermal plug.	Thermal plug.

* J. S. Bogen, Universal Oil Products Company.
† This is the intake air temperature, not mixing temperature.
‡ This ratio must be corrected for barometer.
§ 2½-in. × 4½-in. variable compression cylinder.

bution, carburetion, air-fuel ratio, humidity, and engine conditions. Instantaneous pressures of 1200 psi or higher may occur under knocking conditions; temperatures in the cylinder may then range from 2200° to 2500° C. These conditions are highly significant when oxidation reactions are taking place. As a primary concept, octane ratings may be considered as the oxidation index of a given compound under the combustion conditions prevailing in an engine.

In considering the fundamental structural factors affecting the octane rating of organic compounds, there are a number of generalizations which may be extended to cover other compounds than hydrocarbons. A number of rules were proposed by Lovell, Campbell, and Boyd [4] in the study of hydrocarbons and their relation to anti-knock properties. For the pure hydrocarbons it was found necessary to modify somewhat their first and second generalizations, while consideration of data on the oxidized compounds showed that these rules were applicable to the oxidized class of motor fuels as well.

Rule 1.—The longer the straight chain of carbon atoms contained in organic molecules, the lower the octane rating, with the exception of the alkenes, where ethene has a lower octane rating than the two following hydrocarbons.

The following examples in Tables II, III, and IV show the application of Rule 1 to the hydrocarbons of different series.

TABLE II.

Straight-chain Paraffins, Pure Compounds.

Compound.	Octane rating.	
	C.F.R. A.S.T.M.[3]	Research method.[5]
Methane	110	100
Ethane	104	100
Propane	100	100
Butane	92	95
Pentane	61	58
Hexane	25	34
Heptane	0	0
Octane	−17	—
Nonane	−45	—
Decane	—	−53

The octane ratings given by Smittenberg for the 2-alkenes do not follow the general smoothness of those reported by Lovell, Campbell, and Boyd in their work, nor do these values fall in line with Rule 1 as well as do the paraffins. Table III shows octane ratings for the pure olefins,[3] and Table IV shows octane ratings of the blends of pure olefins with a reference fuel. In general, it may be seen from the data in Table IV, the octane ratings of the blends follow the same trend as the pure compounds.

TABLE III.

Straight-chain Olefins, Pure Compounds.

Compound.	Octane rating,[2] C.F.R. A.S.T.M.
Ethene	81
Propene	85
Butene-2	83 [4]
Pentene-2	80
Hexene-2	78
Octene-2	55

Calculated values of the octane ratings of olefins from aniline equivalents,[4] as well as the direct determination of octane ratings given by Smittenberg, Hoog, Moerbeek, and van der Zijden,[3] show the same trend in lowered rating with increase in chain length. The orientation of the double bond towards the centre of a molecule containing the same number of carbon atoms raises the octane rating.[4] Table IV shows the octane ratings determined on the pure compounds and on the blends of 1 gram mole of hydrocarbon per litre of 55 octane rating reference fuel.

TABLE IV.

Olefin Series,[10] Pure and Blended Compounds.

Compound.	Octane rating.			
	Pure compound.		Blended compound.	
	M.M.	R.M.	M.M.	R.M.
Ethene		100		85·5
Propene		100		102·0
Butene-1	80			111·5
Butene-2	83			
Pentene-1		92		98·5
Pentene-2		98	107	125
Hexene-1		80		85
Hexene-2		89		100
Hexene-3		97		
Heptene-1		54		55
Heptene-2		70		
Heptene-3		84		95
Octene-1		39		25
Octene-2				55
Octene-3				73
Octene-4				91
Nonene-1				15

Data listed for the acetylene hydrocarbons are so scarce that no correlations can be made with the material; however, Table V shows the octane ratings determined for the straight-chain acetylenes, and Table VI shows a comparison of these acetylenes with straight chains to the olefins and paraffins of similar structure.

TABLE V.

Straight-chain Acetylenes, Pure and Blended Compounds.

Compound.	Octane rating, research method.	
	Pure compound.[7]	Blended compound.
Acetylene	80	
Pentyne-2		108 [8]
Heptyne-1	84	76 [9]
Heptyne-3	40	−30 [7]
Octyne-2	66	62 [9]

TABLE VI.

Pure and Blended Compounds.

Compound.	Octane rating, research method.	
	Pure compound.	Blended compound.
Ethane	>100 [7]	
Ethene	>100 [7]	85-5 [9]
Ethyne	80 [7]	
Pentane	58 [11]	60 [9]
Pentene-2	98 [7]	125 [9]
Pentyne-2		108 [8]
Heptane	0 [7]	0 [9]
Heptene-1	54 [7]	55 [9]
Heptyne-1	84 [7]	76 [9]
Heptene-3	84 [7]	95 [9]
Heptyne-3	40 [7]	−30 [7]

While the data presented here are not too conclusive, it seems that the octane-rating effect of the acetylene bonding is intermediate between that of the paraffin bond and the olefin bond.

The pure compounds of the *cyclo*paraffin and aromatic series given in Table VII also follow Rule 1 insofar as the data are given; that is, the length of the substituting straight chain lowers the octane rating.

TABLE VII.

Compound.	Octane rating, C.F.R. A.S.T.M.
*cyclo*Pentane	83 [8]
Methyl*cyclo*pentane	82 [8]
*cyclo*Hexane	77 [8]
Methyl*cyclo*hexane	71 [8]
Benzene	108 [8]
Methylbenzene (Toluene)	104 [8]
Ethylbenzene	96 [12]

The values derived from calculating aniline equivalents in blends for the alicyclic group show the trend even better than those determined for the pure compound. Table VIII shows the octane ratings for the *cyclo*-paraffin series.

TABLE VIII.

cyclo*Paraffin Series*,[10] *Pure and Blended Compounds.*

Compound.	Octane rating, research method.	
	Pure compound.	Blended compound.
*cyclo*Pentane	100	125
Methyl*cyclo*pentane	81·5	71
Ethyl*cyclo*pentane	62	59
Propyl*cyclo*pentane		16
Butyl*cyclo*pentane		−11
Pentyl*cyclo*pentane		−19
*cyclo*Hexane		86
Methyl*cyclo*hexane		74
Ethyl*cyclo*hexane		44
Propyl*cyclo*hexane		20
Butyl*cyclo*hexane		3
Pentyl*cyclo*hexane		−8

Table IX shows *cyclo*-olefines, and here also the effect of chain lengthening is evident.

TABLE IX.

cyclo*Olefin Series*,[10] *Blended Compounds.*

Compound.	Octane rating, research method, blended compound.
*cyclo*Pentene	140
Methyl*cyclo*pentene	143
Ethyl*cyclo*pentene	102
Propyl*cyclo*pentene	96
Butyl*cyclo*pentene	82
Pentyl*cyclo*pentene	63
*cyclo*Hexene	102
Methyl*cyclo*hexene	133
Ethyl*cyclo*hexene	100
Butyl*cyclo*hexene	63
Pentyl*cyclo*hexene	58

The monoalkyl-substituted series of aromatic hydrocarbon blends shows a deviation from Rule 1 on the longer straight-chain lowering of octane ratings. Table X shows that up to propylbenzene the octane rating rises with increasing chain length; beyond the propyl group, however, the normal lowering with progressive chain lengthening[14] is exhibited. This seems to be true only for the blends, since Table VII, on pure compounds, shows the lowering of octane rating with each successive methyl addition to the alkyl substitution group.

TABLE X.

Blended Compounds.[13]

Compound.	Octane rating, research method, blended compound.
Benzene	108
Methylbenzene	120
Ethylbenzene	128
Propylbenzene	137
Butylbenzene	115
Pentylbenzene	101
Heptylbenzene	46

Rule 2.—Branched chain aliphatic compounds have higher octane ratings than the normal compounds.

(*a*) Monomethyl isomers have higher octane rating than the normal compound, and the dimethyl isomers are higher than either the normal or monomethyl isomers, as shown in Table XI.

TABLE XI.

Compound.	Octane rating,[3] C.F.R. A.S.T.M.
Hexane	25
2-Methylpentane	73
3-Methylpentane	75
2 : 2-Dimethylbutane	96
2 : 3-Dimethylbutane	95

(*b*) As the monomethyl substitution approaches the centre of the molecule, the octane rating is increased over that of the other monomethyl substitutions located nearer the end of the chain; for example, 2-methylpentane has an octane rating of 73 and 3-methylpentane a rating of 75 in the group of hydrocarbons shown in Table XII. This is further substantiated in blending values given for 2-methylpentane, 69; and 3-methylpentane, 84.[14] Lovell and Campbell state that centralization of the molecule is the factor increasing the octane rating; however, this is not true in the case of the dimethyl compounds, where one carbon atom contains both methyl substituents.

TABLE XII.

Compound.	Octane rating,[3] C.F.R. A.S.T.M.
2-Methylpentane	73
3-Methylpentane	75

Branching of the side-chains in the olefinic series shows the same effect

as the paraffin branching. The presence of the double bond in its various positions is also seen to influence the octane rating of the olefins.

Tables XIII and XIV show the same effects in the olefin series as were discussed in the paraffin group, with some exceptions showing, due possibly to the type of linkages, and not the structure. Table XIII shows a higher octane rating for peripheral methyl substitutions where the double bonds lie near the centre, in this instance in the 2-position, while for paraffin hydrocarbons the substitution of methyl radical near the centre of the molecule raises the octane rating.

TABLE XIII.

Pure and Blended Compounds.

Compound.	Octane rating.		
	Pure compound, motor method.	Blended compound.	
		Motor method.	Research method.
3-Methylpentene-2 . . .			109 [9]
4-Methylpentene-2 . . .			115 [7]
2 : 4 : 4-Trimethylpentene-2 .	89 [7]	133 [9]	
3 : 4 : 4-Trimethylpentene-2 .	85·6 [15]	72·5 [15]	

The olefin compounds having double bonds in the one position give octane relations more nearly like the paraffins in this instance, since the methyl substitutions near the centre of the molecules give higher ratings as in the paraffin series. Table XIV shows the 1-alkenes in this relation.

TABLE XIV.

Pure and Blended Compounds.

Compound.	Octane rating.			
	Pure compound.		Blended compound.	
	M.M.	R.M.	M.M.	R.M.
4-Methylhexene-1 . .		85 [7]		86 [9]
5-Methylhexane-1 . .		82 [7]		83 [9]
2-Methyloctene-1 . .	74·8 [15]		69·8 [15]	
3-Methyloctene-1 . .	83·5 [15]		72·2 [15]	

Table XV, on the acetylenes, shows a lowering of the octane rating with the orientation of the triple bond towards the centre of the molecule which is directly opposite the effect noted in the case of the olefines.

TABLE XV.

Pure and Blended Compounds.

Compound.	Octane rating, research method.	
	Pure compound.	Blended compound.
Heptyne-1	84 [7]	76 [9]
Heptyne-3	40 [7]	−30 [7]
5-Methylhexyne-1		89 [9]
5-Methylhexyne-2		88 [9]

(*c*) Dimethyl substitutions exhibit the same tendencies as the monomethyl substitutions, as long as the two methyls are on adjacent carbon atoms in the molecule. 2 : 3-Dimethylhexane has an octane rating of 76 and 3 : 4-dimethylhexane has a value of 85. Table XVI shows the ratings in tabular form.

TABLE XVI.

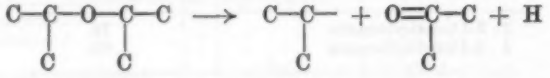
Compound.	Octane rating,[8] C.F.R. A.S.T.M.
2 : 3-Dimethylhexane	76
3 : 4-Dimethylhexane	85

These types of methyl branching introduce tertiary carbon atoms into the molecule, and the effect is one of diminishing the ease of oxidation.[16]

In explaining the higher octane ratings of monomethyl isomers and the rise in rating accompanying the movement of methyl groups towards the centre of the molecule, the thermal behaviour of normal and *iso*butane and of normal and *iso*pentane is relevant.

Under comparable conditions (600–700° C.) *iso*butane dehydrogenates more readily to *iso*butene than *n*-butane to butenes.[17] In the case of normal and *iso*pentane, the *iso*-compound was shown to yield alkenes with the double bond in the inner rather than the terminal position found in the thermal decomposition products of the normal compound.[18] Since the final products of a purely thermal reaction are shown to be olefins, the intermediate products formed at high temperatures and pressures could readily be the free radicals derived from the parent compound. Experimental evidence has shown that the energy required to dissociate the C–C bond is about 21,000 cal. less than that required for the C–H bond break. Dissociation energies for C–C and C–H bonds are 71,000 and 92,000 cal., respectively. In the case of oxidation reactions at explosion temperatures, Sagulin [19] found the heat of activation of the C–H bond to be about 64,000 cal., which accounts not only for the ease of dehydrogenation, but would, in part, explain the much higher octane ratings of the isomeric compounds in relation to the straight chain. Even at explosion temperatures it may be postulated that the momentary formation of the free radicals, *iso*propyl and *iso*butyl, reduces the volume of gases simultaneously released in the engine cylinder. In contrast, there are many more radicals, and hence greater volumes, in the case of the straight-chain compounds.

A plausible explanation for the higher anti-knock rating of the hydrocarbons with the centred methyl would be a split of the hydrocarbon molecule at the tertiary carbon atom, producing an anti-knock effect which would give two, or possibly three, parts of the molecule instituting chain reactions at the same time in contrast to the number of radicals released by the normal compound. The pressure increase set up by the splitting of the molecule gives the knock effect in accordance with the number and kind of hydrocarbon radicals set free. According to Rice's explanation, the pressure existing in the automotive cylinder would be conducive to the formation of free *iso*propyl and *tert.*-butyl radicals.[20] As a further observation it may also be stated that ketones[21] might be reasonably expected under those pressure and temperature conditions existing in the automotive cylinder. Both the oxygen and the hydrocarbon are in an activated state, and in the case of the isomeric hydrocarbons the ketone would also have a higher initial combustion temperature, and therefore greater stability, than the peroxides which are postulated by Lewis and von Elbe.[22] A further explanation might be given in the justification of the high anti-knock rating for *iso*propyl ether, which is 99. In this instance, with one part of the molecule having an oxygen attached, the reaction might be shown to proceed as follows:



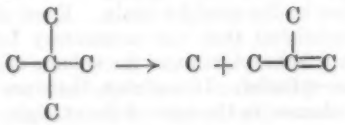
Such a compound would oxidize at the tertiary carbon in one part of the ether, whilst the other part of the ether would have formed a ketone.

Rule 3.—A quaternary carbon atom when oriented towards one end of a hydrocarbon chain increases the octane rating. Table XVII shows the effect of orientation of the quaternary carbon.

TABLE XVII.

Compound.	Octane rating, C.F.R. A.S.T.M.
2 : 2-Dimethylpentane . . .	93 [3]
3 : 3-Dimethylpentane . . .	84 [3]
2 : 2 : 3 : 3-Tetramethylhexane .	97 [23]
3 : 3 : 4 : 4-Tetramethylhexane .	65 [24]

The effect of the quaternary carbon under purely thermal conditions has not been sufficiently studied to give basis to any such hypotheses as were given for the effect of the tertiary carbon. Frey and Hepp[18] found that neopentane decomposed almost quantitatively at 575° C., according to the following reaction:



If this reaction may be applied as affecting other compounds of this type, the initial reaction may be shown as a splitting of the molecule at the quaternary carbon. 2 : 2-Dimethylpentane will possibly react to give either the olefin, or more probably to give the free radicals, thus releasing only two gases in the engine cylinder. The pressure increase set up by such a yield of products of decomposition would be much less than that released by the isomeric 3 : 3-dimethylpentane, and this would explain, in part, the reduced octane rating for the 3 : 3-dimethyl compound. This assumption is based on Rice's [20] statement that under heat and pressure conditions heavier radicals such as *tert.*-butyl and *iso*propyl may momentarily exist. In 3 : 3-dimethylpentane, with the quaternary carbon centred in the molecule, the octane rating is 84, in comparison with 93 for the 2 : 2-dimethyl compound. In view of Rice's explanation of the more radicals set free the higher the initial pressure, it may be shown that three gaseous products would be formed in the case of the 3 : 3-dimethyl compound rather than two as was shown for the 2 : 2-dimethyl compound. The pressure increase thus set up would probably institute the knocking more readily than in the other compound.

Orientation of compacted dimethyl and trimethyl substitutions towards one end of the molecule raises the octane rating as shown in Table XVIII.

TABLE XVIII.

Compound.	Octane rating,[8] C.F.R. A.S.T.M.
2 : 2-Dimethylbutane	96
2 : 3-Dimethylbutane	95
2 : 2-Dimethylpentane	93
2 : 3-Dimethylpentane	89
2 : 4-Dimethylpentane	82
3 : 3-Dimethylpentane	84
2 : 3-Dimethylhexane	76
2 : 5-Dimethylhexane	52
3 : 4-Dimethylhexane	85
2 : 2 : 3-Trimethylpentane	102
2 : 2 : 4-Trimethylpentane	100
2 : 3 : 4-Trimethylpentane	97

Rule 4.—Methyl additions on cyclic structures of a given number of carbon atoms lower the octane rating, whilst methyl additions on a chain of a given number of carbon atoms raise the octane rating, except in the case of *n*-butane to 2-methylbutane, where the octane rating is lowered by adding the methyl substituent. Table XIX shows the relationship.

Rule 5.—In hydrocarbons of the *cyclo*hexyl group the effect of the *ortho*, *meta*, and *para* positions is one of lowering the octane rating as the substituents are more widely separated. The *ortho* position

gives the highest octane rating, and the *para* position gives the lowest. In the benzene series the opposite effect is noted for the *ortho*, *meta*, and *para* positions. Tables XX and XXI show the effect of position for *cyclo*hexane and benzene hydrocarbons.

TABLE XIX.

Compound.	Octane rating,[3] C.F.R. A.S.T.M.
n-Butane	92
2-Methylbutane	89
n-Pentane	61
2-Methylpentane	73
3-Methylpentane	75
n-Hexane	25
2-Methylhexane	45
n-Heptane	0
3-Methylheptane	35
*cyclo*Pentane	83
Methyl*cyclo*pentane	82
*cyclo*Hexane	77
Methyl*cyclo*hexane	71
Benzene	108
Methylbenzene (Toluene)	104

TABLE XX.

Pure and Blended Compounds.[10]

Compound.	Octane rating, research method.	
	Pure compound.	Blended compound.
ortho-1 : 2-Dimethyl*cyclo*hexane	86	75
meta-1 : 3-Dimethyl*cyclo*hexane	77	68
para-1 : 4-Dimethyl*cyclo*hexane	74	75
1-Methyl-2-ethyl*cyclo*hexane	74	55
1-Methyl-3-ethyl*cyclo*hexane	58	34
1-Methyl-4-ethyl*cyclo*hexane	54	27
1-Methyl-2-propyl*cyclo*hexane	49	37
1-Methyl-3-propyl*cyclo*hexane	39	22
1-Methyl-4-propyl*cyclo*hexane	34	20
1-Methyl-2-butyl*cyclo*hexane	39	6
1-Methyl-3-butyl*cyclo*hexane	34	−5
1-Methyl-4-butyl*cyclo*hexane	28	−5

TABLE XXI.

Blended Compounds.[10]

Compound.	Octane rating, research method, blended compound.
ortho-1 : 2-Dimethylbenzene	121
meta-1 : 3-Dimethylbenzene	144
para-1 : 4-Dimethylbenzene	154
1-Methyl-2-ethylbenzene	107
1-Methyl-3-ethylbenzene	130
1-Methyl-4-ethylbenzene	147
1-Methyl-2-propylbenzene	114
1-Methyl-3-propylbenzene	130
1-Methyl-4-propylbenzene	130
1-Methyl-2-butylbenzene	102
1-Methyl-3-butylbenzene	113
1-Methyl-4-butylbenzene	123
1-Methyl-2-amylbenzene	90
1-Methyl-3-amylbenzene	90
1-Methyl-4-amylbenzene	100
1 : 3-Diethylbenzene	145
1 : 4-Diethylbenzene	158

ALCOHOLS, ETHERS, AND KETONES.

Oxidation compounds derivable from the hydrocarbons have been considered for some time as products suitable for motor fuels, and in some instances have been widely adopted, although these compounds have not proved entirely satisfactory. Ketones and ethers have been given some attention, but they have not had as wide application as the alcohols.

The following tables and generalizations show the relative octane rating efficiencies of these compounds.

Rule 6.—With the exception of methyl alcohol, the lengthening of the straight chain of carbon atoms in the alcohol molecule lowers the octane rating.

Table XXII shows the octane ratings of the normal alcohols up to pentyl alcohols.

TABLE XXII.

Alcohols.[11]

Compound.	Octane rating, C.F.R. motor method, pure compounds.
Methyl	98
Ethyl	99
n-Propyl	90
n-Butyl	87
n-Pentyl	78

Up to and inclusive of *n*-butyl alcohol, the effect of the OH radical seems to be one of lowering the octane rating in comparison with the normal hydrocarbons. Pentyl alcohol shows a higher octane rating than *n*-pentane; however, at present there are no data to show whether or not this reversal holds for the remainder of the normal alcohols boiling within the gasoline range.

Isomeric alcohols show that chain branching raises the octane rating, which is in direct agreement with Rule 2 shown previously for the hydrocarbons. Table XXIII shows the *n*-alcohols and their isomers and the effect of chain branching on octane number.

TABLE XXIII.

Alcohols.

Compound.	Octane rating, C.F.R. motor method.[25]
n-Propyl	90
*iso*Propyl	104
n-Butyl	87
*iso*Butyl	88
sec.-Butyl	92
tert.-Butyl	100+
n-Amyl (pentyl)	78
tert.-Amyl (pentyl)	100+

The octane ratings of a number of pure ketones have been determined, and, insofar as the data show, the same rules hold for the ketones as for the alcohols. Table XXIV shows the octane ratings of the ketones.

TABLE XXIV.

Ketones.

Compound.	Octane rating, C.F.R. motor method.
Methyl (acetone)	100
Methylethyl	99
Methylpentyl	80
4-Methyl-3-penten-2-one	91
2 : 6-Dimethyl-2 : 5-heptadien-4-one	78

The two latter compounds in Table XXIV are not strictly comparable to the preceding ones in the table, but they serve to show somewhat the effect of branching and the effect of the double bond; however, there is no method in this instance of determining the separate effect of either type of structure.

The material presented for the ethers is not on the pure compounds, but was taken from 25 per cent. blends of the pure ethers in aviation gasoline of 74 octane number.[26] The figures of over 100 octane number are extrapolated values.

Tables XXV and XXVI show the effect of chain lengthening and chain branching in ethers which is analogous to that of the preceding compounds, with the exception of the ethyl-substituted compound; in each case the octane rating is higher than the methyl compound preceding. There was a slight indication of this phenomenon in the alcohols, but it was not nearly so marked as in the case of the ethers.

TABLE XXV.

Ethers.[26]

Compound.	Octane rating, C.F.R. motor method, blended compound.
Methyl-*iso*propyl	73
Ethyl-*iso*propyl	75
Methyl-*tert.*-butyl	111
Ethyl-*tert.*-butyl	115
n-Propyl-*tert.*-butyl	103
n-Butyl-*tert.*-butyl	81
n-Amyl-*tert.*-butyl	63
Methyl-*tert.*-amyl	108
Ethyl-*tert.*-amyl	112

TABLE XXVI.

Effect of Branched Chain in Ethers.

Compound.	Octane rating, C.F.R. motor method, blended compound.
Ethyl-*sec.*-butyl	63
Ethyl-*tert.*-butyl	115
n-Butyl-*tert.*-butyl	81
sec.-Butyl-*tert.*-butyl	106

From the foregoing tables on the octane rating of alcohols, ketones, and ethers, it is readily seen that these oxygenated compounds follow approximately the same rules on octane rating relationships as the paraffin hydrocarbons.

THERMAL RELATIONSHIPS AND OCTANE RATINGS.

The octane ratings and the relationships due to structure presented for the hydrocarbons are not unique, since other types of constants have shown that thermal stabilities, initial combustion temperature, and critical compression ratios are also characteristic functions of the structure involved, and are lowered with the increased chain lengths.

Rule 7.—The thermal stability of the pure normal paraffins is inversely proportional to the length of the carbon chain.[27]

The following rules are more or less dependent on Rule 6, yet their applicability in engine performance is more readily seen.

Rule 8.—The initial combustion temperature is lowered as the carbon content of the normal paraffin increases.

Table XXVII shows the lowered initial combustion temperatures with increased carbon chain length.

TABLE XXVII.

Lowest Temperatures of Initial Combustion in Air of Normal Paraffin Hydrocarbons Compared to their Octane Ratings.[18]

Compound.	Initial combustion temperature, ° C.	Octane rating.	
		Motor method.	Research method.
Methane . . .	615	125	100
Ethane . . .	542	125	100
Propane . . .	420 *	125	100
Butane . . .	350 *	91	95
Pentane . . .	295	64	58
Hexane . . .	265	59	34
Heptane . . .	230 *	0	0
Octane . . .	215	−28	
Nonane . . .	210	−28	
Decane . . .	210		−53

* These values were interpolated from a curve which was plotted from the other values shown giving temperatures of initial combustion against the number of carbon atoms in the normal paraffin chains.

Rule 9.—The critical compression ratio of the pure normal alkanes is in inverse order to the carbon chain length, *i.e.*, the highest critical compression ratios are for the lower members of the series.

Tables XXVIII and XXIX show the critical compression ratios for the various hydrocarbons as well as the actual operating compression pressures for the test engine and for the automobile engines under approximate test-engine conditions.

TABLE XXVIII.

Paraffins.	Critical compression ratio.	Compression pressure, P.S.I.	
		Actual values C.F.R. engine.	Auto engine under approximate C.F.R. conditions.
Methane . .	15 : 1	349	419
Ethane . . .	14 : 1	323	388
Propane . .	12 : 1	273	327
Butane . . .	6·4 : 1	130	156
Pentane . .	3·8 : 1	67	78
Hexane . .	3·3 : 1	55	66
Heptane . .	2·8 : 1	42	50

TABLE XXIX.

Olefins.	Critical compression ratio.	Compression pressure, P.S.I.	
		Actual values C.F.R. engine.	Auto engine under approximate C.F.R. conditions.
Ethene . . .	8·5 : 1	188	226
Propene . .	8·4 : 1	185	222
Pentene-1 . .	5·8 : 1	115	138
Hexene-1 . .	4·6 : 1	82	98
Heptene-1 . .	2·8 : 1	42	50

SUMMARY.

In summarizing the effect of chemical structures on octane ratings, the combustion conditions under which the octane ratings have been made are the most vital factor in any octane rating given for a chemical compound. The octane ratings given for the various compounds and the generalizations made from them are specific for the test method indicated, and any change in the test method markedly alters the octane rating of the compound.

Universal Oil Products Company,
Research Laboratories,
Chicago, Illinois.

REFERENCES.

1 Lovell, W. G., Campbell, J. M., and Boyd, T. A., *Ind. Eng. Chem.*, 1931, **23**, 26–29.
2 Edgar, G., *ibid.*, 1927, **19**, 145.
3 Smittenberg, J., Hoog, H., Moerbeek, B. H., and van der Zijden, M. J., *J. Inst. Petrol.*, 1940, **26**, No. 201, 294–303.
4 Lovell, W. G., and Campbell, J. M., "The Science of Petroleum," Vol. IV, pp. 3004–3023. Oxford University Press, London, 1938.
5 Doss, M. P., "Physical Constants of the Principal Hydrocarbons," p. 1. The Texas Company, 1939.
6 Neptune, F. B., and Trimble, H. M., *Oil Gas J.*, May 10, 1934, p. 44.
7 Hoffert, W. H., and Claxton, G., "Motor Benzole," end Ed., pp. 640–641. London, 1938.
8 Petrov, A. D., and Azatyan, V. D., *Uspekhi, Khim.*, 1940, **9**, No. 5, 498–521.
9 Lovell, W. G., and Campbell, J. M., "The Science of Petroleum," Vol. IV, pp. 3004–3023. Oxford University Press, London, 1938.
10 Doss, M. P., "Physical Constants of Principal Hydrocarbons." Texas Company, New York City, 1939.
11 Spiers, "Technical Data on Fuel," 2nd Ed., 1934.
12 Octane Number Determination, U.O.P. Co.
13 Lovell, W. G., Campbell, J. M., and Boyd, T. A., Calculated from Aniline Equivalents, *Ind. Eng. Chem.*, 1934, **26**, 475.
14 Lovell, W. G., and Campbell, J. M., "The Science of Petroleum," Vol. IV, pp. 3016–3023. Oxford University Press, 1938.
15 Birch, S. F., *J. Soc. chem. Ind.*, 1936, **55**, 336–337T. (30% blend with 52·5 O.N. base.)
16 Maman, A., *Compt. rend.*, 1937, **205**, 319–321.
17 Hurd, C. D., and Spence, L. U., *J. Amer. chem. Soc.*, 1929, **51**, 3353.
18 Frey, F. E., and Hepp, H. J., *Industr. Engng Chem.*, 1935, **25**, 441.
19 Sagulin, A. V., *Z. physikal. Chem.*, 1928, **1B**, 275.
20 Rice, F. O., *Industr. Engng Chem.*, 1934, **26**, 259.

[21] Pope, J. C., Dykstra, F. J., and Edgar, G. J., *Ann. Chem. Soc.*, 1929, **51**, 1875–1889, 2303–2213.
[23] Lewis, B., and von Elbe, G., "Combustion, Flames and Explosions of Gases," pp. 90–91. Cambridge Press, London, 1938.
[23] Cramer, P. L., and Campbell, J. M., *Industr. Engng Chem.*, 1937, **29**, 234.
[24] Brooks, D. B., Cleaton, R. B., and Carter, F. T., *Bur. Stand. J. Res.*, 1937, **19**, 319.
[25] Universal Oil Products Company Determination.
[26] Hoffman, E., Lapeyrouse, M., and Sweeney, W., "Second World Petroleum Congress," Vol. III, pp. 812–819. Paris, June, 1937.
[27] Egloff, G., "Reactions of Pure Hydrocarbons," p. 7 (1937), A.C.S. Monograph Series No. 73.
[28] Callendar, H. L., and Mardles, E. W. J., *Engineering*, 4th Feb., 1927.

THE INSTITUTE OF PETROLEUM.

A MEETING of the Institute was held at the Royal Society of Arts, London, W.C. 2, at 5 p.m., on Tuesday, March 11th, 1941. The Chair was occupied by Dr. F. H. GARNER.

The following paper was introduced by Dr. A. E. DUNSTAN, and on his proposition it was agreed that a cable should be sent to Dr. Egloff, saying that his paper had been presented that evening and tendering him the thanks of the Institute for it.

"Octane Rating Relationships of Aliphatic, Alicyclic, Mononuclear Aromatic Hydrocarbons, Alcohols, Ethers, and Ketones." By Gustav Egloff and P. M. Van Arsdell. (See page 121.)

DISCUSSION.

THE CHAIRMAN said he was sure all the members present would agree that the authors were to be congratulated on having Dr. Dunstan to present their paper for them, and he wished to propose a vote of thanks to Dr. Dunstan for presenting the paper in his own inimitable manner.

The paper was largely a compilation of the octane ratings scattered throughout the literature of hydrocarbons, alcohols, ethers, and ketones—in fact, practically all the compounds that were likely to be met in motor fuel. The ratings were mainly by the motor method, and, to use Dr. Dunstan's words in introducing the paper, the really important question was what the engine thought of the fuel. To answer that question fully one had to know, of course, not only the rating by the motor method, but also the rating under other engine conditions if satisfactory correlation was to be obtained with actual performance in the motor-car or in the aero engine. For that reason, the American Petroleum Institute had recently sponsored a programme of research on hydrocarbons, and had just published a report of twenty-three pure hydrocarbons, and had employed two different speeds, two different jacket temperatures, two different air temperatures, and different concentrations of lead tetraethyl.

He did not think the authors' statement: "The relation of chemical structure to motor-fuel efficiency was first brought out in 1931, when Lovell, Campbell and Boyd published their work on the combustion properties of aliphatic hydrocarbons," was quite correct, because the work of Ricardo and others preceded that work by a number of years. Actually the work of Ricardo and the work of Boyd and his co-workers in the States were practically contemporary, but it was Ricardo who first investigated the individual hydrocarbons present in motor fuels, particularly benzene, toluene, and xylene, which was included in the Empire Motor Fuels Committee Report published in 1924. This was supplemented later by an investigation made into cracked fuels under the auspices of the Institution of Automobile Engineers.

THE CHAIRMAN then read the following comments by the President, Professor Nash:—

"The paper by Messrs. Egloff and Van Arsdell is a very interesting one indeed, and I do not envy Dr. Dunstan the task of having to present it to the members of the Institute.

There are a few point I should like to raise, and the first one is in connection with Table III, where it will be noticed there is a diminution from hexene-2 octane rating 78 to octene-2 octane rating 55, that is, a difference of 23 octane numbers, which does not fall into line with the diminution of octane rating from propene upwards. It causes one to doubt the purity of the octene-2 and to suggest that the double bond is probably nearer to the centre of the molecule.

With regard to Table VI, the first heptyne-1 should undoubtedly read heptene-1. With the C_3 hydrocarbons it will be noticed that there is a decrease of the octane rating in the blended compound, whereas with the C_7 hydrocarbons there is an increase. It is very difficult to prove the position of the triple and double bonds, and causes one to query again the purity of the substances tested.

In the paragraph preceding Table VIII reference is made to aniline equivalents in blends, and I should like to ask whether this method has been proved to be an accurate one. It would also be interesting to know in the *cyclo*-olefine series in Table IX where the position of the double bond is. A comparison is also made between Table X and Table VII, the former being for blended compounds and the latter for pure compounds. As there would be a difference here in the primary products of combustion, could one expect these two tables to be exactly comparable?

In the case of Table XIII centralization of the methyl radical appears to decrease the octane rating, whereas when it is in the peripheral position the octane rating increases. The reverse, however, is the case with the compounds in Table XIV. Can we make a generalization out of the data available, which rather suggests in regard to Table XIV that the compounds are acting oppositely? In regard to Table XVIII can one differentiate between an octane rating of 96 and 95? In Rule 5 hydrocarbons of the *cyclo*-hexyl (*sic*) group are compared with the benzene series. This rule is not so remarkable when one bears in mind that the two cyclic groups are entirely different. Again, one would ask whether, as in Table XXIII, one can differentiate the behaviour of the *n*-butyl and *iso*-butyl alcohols when the octane ratings are 87 and 88 respectively."

Dr. A. E. Dunstan said that it had struck him that some of the figures might be open to some misapprehension, because before the combustion process, as the authors pointed out, the hydrocarbon or alcohol or ketone might be subjected to very high temperatures; the authors mentioned 2200° C. He did not know whether that was a justifiable temperature, in the sense that it was uniform throughout the mixture.

The Chairman said it was quite feasible.

Dr. Dunstan suggested that there was therefore a very great possibility of isomerization taking place; at any rate, he thought that was a point which should be borne in mind. Did the authentic chemical entity exist under such conditions or was it changed?

Dr. E. B. Evans regretted that he had not yet had the opportunity to study Dr. Egloff and Mr. van Arsdell's interesting paper in detail. There were no points which he himself wished to raise at the moment, but he noticed that Professor Nash had raised a question as to the accuracy of the method of calculating blending octane numbers from aniline equivalents.

This calculation, which enabled Campbell, Lovell, and Boyd's results to be expressed in terms of octane numbers, was made about 1932, and published in a paper by Dr. Garner and others (Garner, Evans, Sprake, and Broom, *Proceedings of World Petroleum Congress*, 1933, p. 170). The aniline equivalents were determined by an engine and method approximating to the old C.F.R. Research Method, using for the blends a base fuel of octane number 55. Knowing the blending octane numbers and aniline equivalents of *n*-heptane and *iso*-octane, two straight lines were drawn giving the relation between the blending octane numbers and aniline equivalents of 20 per cent. volume solutions of these hydrocarbons. A number of the hydrocarbons for which aniline equivalents had been recorded by Campbell, Lovell, and Boyd had also been examined for blending octane number on the S. 30 engine at 212° F. jacket temperature, by ourselves. The S. 30 procedure is very similar to the old C.F.R. Research

Method, and plotting the data from the two sources showed that most of the points fell very near to the two straight lines obtained from heptane, *iso*-octane, and the reference fuel. Full details of the method of conversion are given in the paper referred to, and the indications are that there is considerable justification for the converted values.

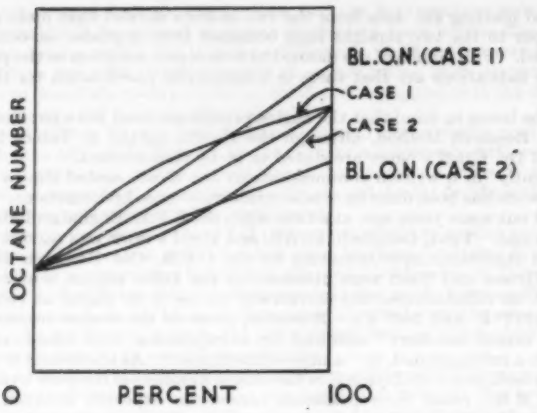
It must be borne in mind that the engine procedures used were not exactly those of the C.F.R. Research Method, although the results quoted in Tables IV, VII, IX, etc., etc., of Dr. Egloff's paper are stated to be by that method.

Subsequently (in a written communication) Dr. Evans stated that a considerable amount of work has been done on octane numbers of pure hydrocarbons. Most of this was carried out some years ago, at a time when the C.F.R. Engine and Motor Methods were not in use. Thus, Campbell, Lovell, and Boyd's work was carried out using an engine and conditions approximating to the C.F.R. Old Research Method. The results of Howes and Nash were obtained on the Delco engine, whilst the work of Garner and his collaborators was carried out on the S. 30 engine at two jacket temperatures (212° F. and 300° F.). Moreover, most of the earlier results were either "blending octane numbers" obtained by extrapolation from blends of the hydrocarbon with a reference fuel, or "aniline equivalents." As the results of Smittenberg, Hoog, Moerbeck, and v. d. Zijden give the octane numbers of the pure hydrocarbons by the C.F.R.M.M., exact correspondence cannot be expected between the various figures quoted by Dr. Egloff and Mr. van Arsdell. This is particularly so in the cases of aromatic and unsaturated hydrocarbons, where the curves of octane number against percentage hydrocarbon in the reference fuel are far from linear. Table XX for naphthene hydrocarbons also illustrates the differences that may be obtained. As in general the concentration of individual hydrocarbons does not exceed a small percentage, except where aromatic or *iso*-paraffin hydrocarbons are used as blending agents, the "blending octane number" is of more practical significance than the rating of the pure hydrocarbon, when considering the usual type of fuel, whilst the values for certain pure hydrocarbons assume importance in connection with aviation fuels of high octane number. Having regard to the different techniques of determination and methods of expression of results employed, it is gratifying to find that the general rules relating knock-value and structure hold as widely as they do.

Dr. A. J. V. Underwood agreed that the authors and Dr. Dunstan had rightly stressed the dependence of the octane number on the conditions of test. This was clearly shown by a comparison of Tables VII and X. In Table VII the figures for benzene, methylbenzene, and ethylbenzene were given as 108, 104, and 96, respectively. In Table X, using a different method of rating and giving blending values, the corresponding figures were 108, 120, and 128. Thus the value for benzene remained unchanged at 108 in the two different tests, whilst the *value* for ethylbenzene rose from 96 to 128. To express it quantitatively very roughly, ethylbenzene was some 20 per cent. better than benzene, according to Table X, whilst according to Table VII it was 10 per cent. worse than benzene. Again, in Table XIII the figures for 2 : 4 : 4-trimethylpentene-2 and for 3 : 4 : 4-trimethylpentene-2 were given as 89 and 85·6 respectively for the pure compound, using the motor method, whilst for the blended compound, using the same method, the corresponding figures were 133 and 72·5. There might be another factor apart from the different test conditions—namely, even though they were presumably using the same method. He thought the decimals might well be omitted in quoting these octane ratings, as they suggested a degree of accuracy which was not justified.

Mr. J. S. Jackson commented on the fact that octane numbers such as 74·8, 69·8, 72·2 appeared in the paper. Such published figures tended to give a rather false impression of the accuracy attainable with the C.F.R. engine, and he felt that these figures should have been rounded off and reported as 75, 70, and 72, respectively. He also pressed for the general acceptance of one method of test for the determination of octane numbers.

The Chairman thought the explanation of the point raised by Dr. Underwood was to be found partly in the shape of the octane number curves of blends of hydrocarbons.



Blending curves may be (1) above, or (2) below a straight line joining the octane number of the two hydrocarbons or (3) a straight line joining the two octane numbers. With hydrocarbons of type 1 the blending octane number is higher than that of the straight hydrocarbon, with type 2 lower, and with type 3 the same. This subject was fully discussed in a paper before the World Petroleum Congress in 1933. (The Blending Octane Numbers of Pure Hydrocarbons and their Dependence upon Concentrations: by Garner, Evans, Sprake, and Broom.)

THE CHAIRMAN said that any written contributions to the discussion which were sent in to the Institute would be forwarded to Dr. Egloff, who would reply to them as well as to the remarks which had been made that evening.

The vote of thanks to Dr. Dunstan was carried unanimously, and the meeting then terminated.

STUDIES ON THE SEPARATION OF PARAFFIN WAXES.

PART IV.—THE SWEATING OF WAX-OIL MIXTURES.*

By M. F. Sawyer, Ph.D., A.M.Inst.Pet., T. G. Hunter, D.Sc., F.Inst.Pet., and A. W. Nash, M.Sc., F.Inst.Pet.

It has been indicated previously [3] that an investigation of the factors affecting the efficiency of the sweating process in which the same oil and wax stock, and also the same sweater, are used throughout, resolves itself into a consideration of the effects of the following variables :—

(1) The amount of oil in the oil–wax mixture,
(2) The rate of sweating,
(3) The rate and extent of the cooling of the oil–wax mixture before commencing to sweat, and
(4) The viscosity of the oil.

No account of experiments on the sweating of synthetic oil–wax mixtures has so far appeared in the technical literature. An objection to the use of such mixtures is that they are not obtained directly from the crude in the relative amounts in which they are blended. The composition of the stock is, however, immaterial, as it is possible that such a stock could be obtained from a crude. Moreover, there are certain definite advantages attending the use of synthetic mixtures.

Complications due to the variations in composition of the waxes and oils present in the mixture, such as might be encountered when using distillates of different boiling ranges, are eliminated. There is also no longer the necessity for the determination of the oil content of the stock—a matter of some difficulty. In the present instance the possible yields of the various melting-point waxes that may be obtained from the wax stock are already known from the previous fractional melting experiments. Finally blends of any desired oil content may be prepared very easily.

Oil Stock.

The stock of dewaxed oil, which was, of course, essential for this series of experiments, was prepared in the following manner. Dewaxed Second Cooled Blue Oil from the Llandarcy Refinery of the Anglo-Iranian Oil Co. was used as the starting material for the preparation. This oil had been removed from the wax distillate cut by filter pressing at a temperature of 13° F. during the normal refinery processing of the distillate, and was further dewaxed in the laboratory with ethylene dichloride at −30° C., using a leaf-filter type dewaxing apparatus.

The oil-solvent mixture containing one volume of oil to two volumes of

* Paper received 23rd January, 1941.

solvent was cooled to −30° C., and then filtered from the wax deposited at this temperature. The solvent was removed from the oil by distillation under reduced pressure with a continuous stream of nitrogen passing through the liquid. The wax-free oil had the following properties:—

Specific gravity at 60° F. . .	0·8960
Refractive index at 60° F. .	1·4867
Cloud point	Below −5° C.
Viscosity:—	
Redwood I at 100° F. . .	64·1 secs.
Redwood I at 140° F. . .	46·7 secs.

Wax Stock.

The wax stock was that of melting point 122·1° F. used in the experiments on fractional melting described in previous publications.[2, 3]

Effect of Oil Content.

In order to investigate the effect of oil content on the sweating operation, six synthetic wax–oil mixtures containing respectively 2, 5, 10, 20, 30, and 40 per cent. by weight of oil were prepared.

The desired amounts of wax and oil were weighed into a beaker. The mixture was then liquefied, thoroughly stirred, and the sample prepared in the sweater as previously described.[3] A sweating rate of 5 per cent. per hour was employed. This rate, besides being likely to lead to satisfactory results, was also quite convenient, as it enabled a sweating run to be completed in two days. The temperature of the sample in the sweater was gradually increased from room temperature, the time elapsing before the collection of the first drops of liquid phase being dependent on the amount of oil in the sample. This is illustrated in Table I.

Table I.

Oil content of sample, %.	First drops of liquid phase after.	Temperature of mass, ° F.
2	210 mins.	101
5	180 ,,	81
30	30 ,,	69
40	10 ,,	65

From the stage at which the first drops of liquid appeared, the heating was adjusted so that sweating proceeded at the desired rate. For the wax–oil mixtures of higher oil content only slight heating was required to maintain the rate during the collection of the first 10 per cent., and during this period it was occasionally found necessary to cut off the current for intervals of a few minutes.

The last 5 per cent. (or less) was removed from the sweater as in the experiments[3] with oil-free wax. Difficulty was also experienced in this

series of experiments in maintaining the desired rate of sweating during the fractionation of the last 10 per cent.

The sweats were collected, in general, in cuts of 5 per cent. by weight, and the melting point of each fraction of melting point higher than 100° F. was determined in the manner previously described. The melting points of fractions lower than 100° F. were not determined accurately, as the melting point method developed for this work, like the I.P.T. and A.S.T.M. methods, is not satisfactory for mixtures of oil and wax containing large amounts (greater than 50 per cent.) of oil. A rough determination was made in some instances, but a knowledge of these low melting points was not considered essential for this investigation. The refractive index at 60° C. was also found for each fraction, using the Abbé Refractometer.

In this series of experiments, as in those with oil-free wax, it is necessary to know the melting point and yield of wax, or oil–wax mixture, present in the sweater at any stage of the experiment. The fractions were therefore blended as before—starting with the last two collected—and the melting point, and also the refractive index at 60° C., found after the addition of each two consecutive fractions. Owing to the presence of oil, the relationship [1] $T = \frac{414{\cdot}5M}{94{\cdot}5 + M}$ cannot be applied to the calculation of melting points, except for those fractions collected after the removal of all the oil.

It was found that the presence of oil rendered the sweating much easier to control than in the experiments with oil-free wax. Little difficulty was experienced in reducing the temperature gradient in the wax–oil mass to 1° F., even in the stock containing only 2 per cent. oil.

This observation is of importance, as it is probable that any difficulties experienced with the laboratory sweater would be increased with industrial plant. It is possible that the presence of oil modifies the crystal structure of the wax in such a manner that sweating is facilitated. Other possible explanations may, however, be suggested. For example, if the surface tension between solid and liquid wax is greater than that between solid wax and oil and if the viscosity of the oil is lower than that of the liquid wax, the oil would flow more easily through the channels that are formed in the wax mass. Some evidence for the existence of these channels was found during the preparation of an oil–wax sample for one of the sweating experiments. The molten wax had been weighed into a beaker and had been cooled to a semi-solid state, such that when the oil was poured on to its surface it did not immediately percolate through. After standing for 1 hour, however, the oil had passed through the mass, leaving the top surface with a honeycomb structure. This observation suggests that sweating may take place through capillary action and that these capillaries or channels are more easily formed when oil is present.

Owing to the large difference between the refractive indices of the dewaxed Second Cooled Blue Oil ($n_D^{60} = 1{\cdot}4867$) and the various waxes obtained in the experiments ($n_D^{60} = 1{\cdot}4327 - 1{\cdot}4372$), the value of n_D^{60} for a wax–oil blend gives an indication of the oil content. The refractive indices of various blends of the dewaxed Second Cooled Blue Oil and the wax stock of melting point 122·1° F. are given in Table II.

TABLE II.

Wax, Weight %.	Oil, Weight %.	n_D^{60}
100	0	1·4342
98	2	1·4350
95	5	1·4367
90	10	1·4386
80	20	1·4434
70	30	1·4486
60	40	1·4536
50	50	1·4589
30	70	1·4696
0	100	1·4867

A graph of oil content/n_D^{60}, covering the range 0–50 per cent. oil, is linear. This linear relationship was used as a means of ascertaining the approximate oil content of this series of experiments.

It was found that the refractive index of the material (wax–oil) remaining in the sweater decreased during the removal of the first fractions, reached a minimum value, and then increased. The percentage of the material (wax–oil) in the sweater at the stage corresponding with the minimum value of the refractive index is given for each run in Table III.

TABLE III.

Run No.	20.	16.	12.	13.	14.	15.
Oil content of stock, %	2	5	10	20	30	40
Minimum n_D^{60}	1·4346	1·4344	1·4347	1·4351	1·4358	1·4366
Stock in sweater, %	70	60/65	50	40	25	5

The position of the minimum refractive index corresponds to the stage at which the removal of the oil is almost complete, and it is seen from Table III above that the yields of nearly oil-free wax, independent of melting point, that may be obtained from the oil–wax mixture, depend on the original oil content of the latter.

The stage at which the oil has been almost completely removed from the stock is indicated in Fig. 1, in which the melting point is plotted against the refractive index at 60° C. for each of the single liquid phase fractions of melting point higher than 100° F. obtained in runs 12–16 and 20. The corresponding graph for the fractions obtained when using oil-free wax stock (Run 8) is also shown. The curve for each run approaches this latter curve as the melting point of the fraction increases, until a stage is reached at which the two curves meet and then become almost coincident. It is suggested that the two curves meet in each instance at the stage where the oil content of the wax present in the sweater is somewhat less than 1 per cent.

This figure of 1 per cent. was estimated as follows. It has been shown in Table II that the addition of 1 per cent. dewaxed Second Cooled Blue Oil to a wax of melting point 122·1° F. increases the refractive index of the latter by approximately 0·0005. It will be appreciated that the

melting points of the waxes under consideration are higher than 122·1° F., but the error introduced by applying this linear relationship to such higher melting waxes is probably negligible, in view of the small difference in the refractive indices of waxes of melting points 120° F. and 140° F., compared with the refractive index of the oil. It was therefore assumed that the addition of 1 per cent. oil increases the refractive index of wax of melting point within this range by approximately 0·0005, an amount which could easily be detected with the Abbé Refractometer. It is seen from Fig. I that the curve for the fractions of corresponding melting points collected after the stage at which the curve for the run meets that for the

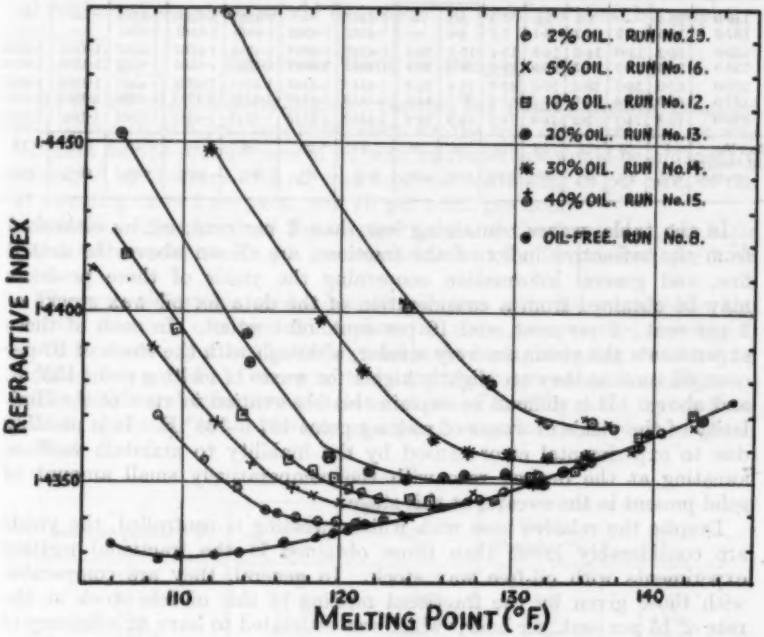


FIG. 1.

oil-free stock (Run No. 8) does not deviate from the latter by more than 0·0002 in refractive index. It may therefore be concluded that the oil contents of fractions in this region are probably less than 1 per cent. It is of interest to note from Fig. 1 that the curve for the wax stock originally containing 40 per cent. oil approaches, but does not meet, the curve for the oil-free stock (Run No. 8). It is therefore to be inferred that, under the particular conditions of sweating employed in this investigation, it is not possible to obtain a substantially oil-free wax from stocks containing 40 per cent. or more oil.

Yield, melting point, and refractive index data are given in Table IV for waxes of various melting points higher than 125° F., the yields being

expressed as a percentage of the total wax present in the original wax–oil stock. The yields and refractive indices of the corresponding waxes obtained from oil-free wax (Run No. 8) are also included. The refractive indices for the blended fractions in the run were calculated from those of the single fractions assuming refractive index to be additive over the small melting point range involved.

TABLE IV.

Melting point, ° F.	Yield, per cent. by weight. Calculated as per cent. of wax present in the wax-oil stock.							Refractive index at 60° C. (n_D^{60}).						
140·0	10·4	—	3·2	3·0	3·0	3·3	—	1·4367	—	1·4367	1·4366	1·4368	—	—
137·5	16·5	5·3	6·7	8·1	7·7	8·9	—	1·4362	1·4362	1·4361	1·4361	1·4361	—	—
135·0	24·2	13·0	14·3	14·8	13·4	12·1	10·1	1·4357	1·4357	1·4356	1·4357	1·4357	1·4361	1·4366
132·5	34·4	23·5	25·3	23·9	25·2	26·0	25·8	1·4352	1·4352	1·4351	1·4352	1·4353	1·4358	1·4369
130·0	47·0	36·7	38·4	37·2	43·7	43·4	36·3	1·4347	1·4348	1·4347	1·4348	1·4351	1·4358	1·4383
127·5	61·5	53·4	53·9	54·7	61·2	57·7	44·2	1·4345	1·4346	1·4346	1·4347	1·4353	1·4368	1·4398
125·0	78·8	74·7	73·2	74·6	75·2	68·9	52·2	1·4342	1·4345	1·4345	1·4349	1·4362	1·4383	1·4412
Run No. .	8	20	16	12	13	14	15	8	20	16	12	13	14	15
Oil content of stock	0%	2%	5%	10%	20%	30%	40%	0%	2%	5%	10%	20%	30%	40%

In the table, waxes containing less than 1 per cent. oil, as estimated from the refractive index of the fractions, are shown above the dotted line, and general information concerning the yields of these products may be obtained from a consideration of the data for oil–wax stocks of 2 per cent., 5 per cent. and 10 per cent. oil content. In each of these experiments the yields are very similar, although with the stock of 10 per cent. oil content they are slightly higher for waxes of melting point 135° F. and above. It is difficult to explain this observation in view of the similarity of the yields of waxes of melting point 127·5–135° F. It is possibly due to experimental error caused by the inability to maintain uniform sweating at the desired rate with the comparatively small amount of solid present in the sweater at this stage.

Despite the relative ease with which sweating is controlled, the yields are considerably lower than those obtained in the fractional melting experiments with oil-free wax stock. In general, they are comparable with those given by the fractional melting of this oil-free stock at the rate of 15 per cent. per hour,[3] which was estimated to have an efficiency of 78 per cent. compared with the assumed 100 per cent. efficiency of Run No. 8. Fractional melting at the rate of 5 per cent. per hour was estimated on the same basis to be 90 per cent. efficient. Otherwise expressed, the yields of substantially oil-free (less than 1 per cent.) waxes of melting point 127·5° F. and above, obtained from the wax–oil stock containing 2–10 per cent. oil, are in the region of 10–12 per cent. lower than those of corresponding melting point obtained under the same conditions by the fractional melting of the oil-free wax stock.

It is apparent that for products of melting point 127·5° F. and above the addition of 2 per cent. oil to the oil-free wax stock has much the same effect as 10 per cent. For products of lower melting point there is a difference, however, for their oil contents vary with the amount of oil initially present in the wax stock.

In view of the comparatively poor yields of lower-melting-point wax obtained from the oil–wax stock of 40 per cent. oil content, and also the failure to obtain a substantially oil-free wax of any melting point from this stock, it is suggested that an oil content of 40 per cent. is above the maximum for satisfactory sweating.

Assuming that one of the objects of sweating is to produce a substantially oil-free scale wax of melting point at least 127·5° F., there seems to be no advantage gained by reducing the oil content of the stock below 10 per cent. Also, as the yield of this oil-free product from a stock containing 20 per cent. oil is relatively much lower than from one containing 10 per cent. oil, it is concluded that for satisfactory and efficient sweating the oil content of the stock should be reduced to 10–12 per cent. by weight.

Effect of Rate of Sweating.

As the effect of the sweating rate variable has already been investigated and discussed in a previous publication for the case of oil-free wax, it was felt that for the present case of oil–wax mixtures this would be sufficiently examined by two runs with oil–wax mixtures containing 10 per cent. of oil, at sweating rates 5 per cent. and 10 per cent. per hour.

Run No. 12 supplied all the necessary data at the 5 per cent. per hour rate, and a new run, No. 21, was carried out at the 10 per cent. per hour rate.

The wax-oil sample containing 10 per cent. oil was prepared in the normal manner, cooling taking place at room temperature overnight. The temperature gradient in the wax–oil mass during sweating could not be reduced below 2° F. Otherwise the experiment proceeded normally.

The yields and refractive indices of waxes of melting point higher than 125° F. remaining in the sweater at a given stage for these runs are given in Table V.

Table V.

Melting point, ° F.	Yield, Weight %.	n_D^{60}.	Yield, Weight %.	n_D^{60}.
140	2·7	1·4366	3·0	1·4367
137·5	7·3	1·4361	6·6	1·4363
135	13·3	1·4357	12·9	1·4359
132·5	21·5	1·4352	22·2	1·4356
130	33·5	1·4348	33·5	1·4353
127·5	49·2	1·4347	48·8	1·4352
125	67·2	1·4349	66·4	1·4356
Run No. . .	12		21	
Oil content of stock	10%		10%	
Rate . . .	5% per hour		10% per hour	

Inspection of the above figures shows that, within experimental error, the yields are the same in each run, although the waxes of melting point below 135° F. from the run at the faster rate are of slightly higher oil content than those of corresponding melting point from the slower run. As there is no doubt that the yield of wax of a given melting point obtained from an oil-free wax stock is dependent on the rate of fractional melting,

the similarity of the yields obtained in the two experiments under consideration is therefore rather unexpected. It is possible, however, that sweating at a rate considerably slower than 5 per cent. per hour would lead to increased yields of the various waxes.

Effect of Method of Preparing Sample.

Two runs were made for the purpose of investigating the extent to which the efficiency of the process is affected by the way in which the wax–oil sample is prepared prior to sweating. Wax–oil mixtures containing 10 per cent. oil were used in these experiments.

Partial Cooling.

The sweater was prepared in the normal manner and the wax–oil sample introduced at a temperature of 130° F. Cooling took place in the absence of draughts until the central region of the mass was at a temperature of 87° F. At this stage a temperature gradient of 4° F. existed in the mass. The cellophane was removed from the outer surface of the sweater, and the latter placed inside the external heater, which had been heated so that the temparature of the air inside was 80–83° F. Sweating at the rate of 5 per cent. per hour was then conducted in the normal manner, the initial drops of liquid appearing in the collecting beaker after 10 minutes' heating.

Shock Cooling.

The sweater was prepared in the normal manner and the wax–oil sample introduced at a temperature of 135° F. The sweater and contents were immediately plunged into an acetone-solid CO_2 bath cooled to −50° C. The bath temperature quickly rose to −25° C. and was maintained at −25° C. to −30° C. for 1 hour whilst the wax–oil sample solidified. On removal from the cooling mixture, the central region of the mass was at a temperature of 55° F. The sample remained at room temperature overnight, and sweating at the rate of 5 per cent. per hour was commenced on the following day.

The sweating appeared to proceed normally in each instance.

The yields and refractive indices of various waxes of melting point higher than 125° F. remaining in the sweater at given stages are given for Runs 18 and 19 in Table VI. The corresponding figures for waxes obtained from the same stock at the same rate of sweating after preparation of the sample in the usual manner (Run No. 12) are included for comparative purposes.

It may be observed that the yields of waxes of the same melting point obtained in the three runs are not very different. There is, however, an indication that the yields of waxes of melting point 135° F. and above are slightly higher in the experiment involving normal cooling of the sample.

The slightly lower yields in the experiment involving partial cooling might possibly be attributed to the wax crystals not having been allowed sufficient time in which to attain the size of those formed during normal cooling to room temperature (Run No. 12).

TABLE VI.

Melting point, ° F.	Normal cooling.		Partial cooling.		Shock cooling.	
	Yield, Weight %.	n_D^{60}.	Yield, Weight %.	n_D^{60}.	Yield, Weight %.	n_D^{60}.
140	2·7	1·4366	—	—	—	—
137·5	7·3	1·4361	6·5	—	5·0	1·4364
135	13·3	1·4357	10·2	1·4360	12·0	1·4359
132·5	21·5	1·4352	20·4	1·4355	22·2	1·4355
130	33·5	1·4348	34·6	1·4352	34·9	1·4352
127·5	49·2	1·4347	50·5	1·4351	50·5	1·4353
125	67·2	1·4349	67·6	1·4353	66·7	1·4356
Run No. .	12		18		19	
Oil content of stock .	10%		10%		10%	
Rate . .	5% per hour		5% per hour		5% per hour	

Rapid or shock cooling would almost certainly cause the formation of very small crystals, especially in the region of the wax–oil mass near the surface of the sweater, where the cooling conditions are most severe.

The refractive index data indicate that the residual waxes of melting point 125° F. and higher, present in the sweater at any given stage in these two runs, contain slightly more oil than those of the same melting point obtained in Run No. 12. It may be inferred from this observation that partial, as well as shock, cooling of the wax–oil sample causes the formation of small wax crystals, which are of such a nature that oil is less easily removed from them during the process of sweating.

The variations in the yields and refractive indices are not, however, sufficiently great to allow any very detailed conclusions to be reached.

It is clear, however, that the rate and extent of cooling of the sample prior to sweating have little effect on the efficiency of the process.

EFFECT OF VISCOSITY OF THE OIL.

Oils of different viscosity for use with the oil-free wax stock in a study of the effect of oil viscosity on the sweating process, may be obtained as follows :—

(i) the viscosity may be varied by employing various oils of different boiling ranges, or

(ii) the desired viscosity may be obtained by blending two dewaxed oils of high and low viscosity respectively.

The use of oils of different boiling ranges introduces complications due to the variation in chemical composition, and it was therefore decided to prepare oils of the desired viscosities from two stocks of dewaxed oils. This method ensures that the same constituents are present in each blend, although, of course, in different proportions.

OIL STOCKS.

The dewaxed Second Cooled Blue Oil, used in the previous experiments, constituted the stock of low viscosity.

The high-viscosity stock was prepared from a Master Lubricant oil supplied from the Anglo-Iranian Oil Co.'s Llandarcy Refinery.

The Second Cooled Blue Oil is obtained from the crude by cold pressing the light wax distillate, and the Master Lubricant is a dewaxed heavier distillate taken from the crude immediately following the light distillate. This heavier distillate was dewaxed on the refinery, using the Sharples process, but it was further dewaxed in the laboratory with ethylene dichloride at −25° F. by the method already described for the Blue Oil. The laboratory dewaxing resulted in a very sticky or resinous oil having the following properties:—

Specific gravity at 60° F.	1·010
Pour point	20° F.
n_D^{60}	1·5587
Viscosity:	
Redwood II at 100° F.	4323 secs.
Redwood II at 140° F.	438·6 secs.

Blends covering a considerable viscosity range could therefore be prepared from these two stocks, and it was proposed to investigate the effect of oils over the complete viscosity range. However, the scheme was interrupted after completion of only two runs, the results of which are now discussed.

In view of the findings in the experiments with oil–wax stocks, it was decided to employ stocks of 10 per cent. oil content. In each instance the sample was prepared in the normal manner, and sweating was conducted at the rate of 5 per cent. per hour. No difficulty was encountered with either stock.

The yields and refractive indices of various waxes of melting point higher than 125° F. remaining in the sweater at given stages are recorded in Table VII. For purposes of comparison, the corresponding figures for Run No. 12 are included.

TABLE VII.

Melting point, ° F.	10% D.B.O.		9% D.B.O. + 1% D.M.L.		7% D.B.O. + 3% D.M.L.	
	Yield, Weight %.	n_D^{60}.	Yield, Weight %.	n_D^{60}.	Yield, Weight %.	n_D^{60}.
140	2·7	1·4366	5·0	1·4368	3·5	1·4369
137·5	7·3	1·4361	10·0	1·4364	7·8	1·4365
135	13·3	1·4357	16·4	1·4359	13·8	1·4361
132·5	21·5	1·4352	25·5	1·4355	23·2	1·4356
130	33·5	1·4348	37·2	1·4353	34·6	1·4353
127·5	49·2	1·4347	52·2	1·4353	47·8	1·4354
125	67·2	1·4349	67·0	1·4355	63·7	1·4357
Run No.	12		22		23	
Rate	5% per hour		5% per hour		5% per hour	

D.B.O. = Dewaxed Blue Oil.
D.M.L. = Dewaxed Master Lubricant.

The experimental data are insufficient for any general conclusions to be stated relating to the effect of the viscosity of the oil on the efficiency of the sweating process. However, the minimum values of n_D^{20} for Runs 22 and 23 are higher than for Run 12 and, moreover, correspond with a higher percentage of residual wax (wax–oil) in the sweater than for Run 12. These observations indicate that the oil of higher viscosity is more difficult to remove from the wax.

In addition to the above experiments with oils of different viscosities, a run was made with a wax–oil mixture consisting of :—

70 per cent. oil-free wax, 15 per cent. D.B.O. and 15 per cent. kerosine (sp. gr. at 60° F. = 0·8025).

The sample was prepared in the usual manner, and sweating was carried out without difficulty at the rate of 5 per cent. per hour.

The comparison of the yields of various waxes obtained in this run with those obtained in Run No. 14, in which the oil–wax stock contained 30 per cent. Dewaxed Blue Oil, is given in Table VIII.

TABLE VIII.

Melting point, ° F.	Yield.	Per cent. by weight.
140	2·4	—
137·5	6·2	—
135	8·5	4·8
132·5	18·2	18·6
130	30·4	28·2
127·5	40·4	35·2
125	48·2	39·8
Run No. . . .	14	17
Oil content of stock .	30% D.B.O.	15% D.B.O. 15% Kerosine

The results of this run are included in order to mention the significance of the comparatively low yields of waxes of melting points 125° and 127·5° F. obtained.

These low yields may be attributed to the higher solubility of the wax in the Blue Oil–Kerosine blend than in the Blue Oil alone. It is therefore suggested that any study of the effect of viscosity should be made in conjunction with experiments on the solubility relationships of the wax and the various oil blends employed.

CONCLUSIONS.

(1) The sweating of an oil–wax mixture is considerably easier to control than the fractional melting of an oil-free wax. This is of particular importance industrially, as ease of control of a process, especially on the commercial scale, is very desirable.

(2) The yields of the various melting-point waxes, calculated as a percentage of the wax content of the oil–wax stock, are considerably

lower than for the corresponding waxes obtained by the fractional melting of the oil-free wax stock at the same rate.

(3) Under the same conditions of sweating, the efficiency of the process is dependent on the oil content of the stock. Little or no advantage is to be gained by de-oiling the stock to an oil content of less than 10 per cent. Also, the most satisfactory sweating stock contains 10–12 per cent. oil. At the other extreme, it is evident that an oil content of 40 per cent. is above the maximum for efficient and satisfactory sweating.

It will be appreciated, however, that these deductions are based on the results of experiments conducted at the same rate of sweating. It is possible, therefore, that a stock containing 40 per cent. oil could be satisfactorily processed at a considerably slower rate, especially during the collection of the first few fractions, when the loss of wax—due to solubility in the oil—would be reduced.

(4) The rate and extent of cooling of the sample prior to sweating have little effect on the yield and oil content of the various waxes produced.

(5) For corresponding melting points, the yields of waxes obtained by sweating at 5 per cent. and 10 per cent. per hour are similar, but those from the faster process are of slightly higher oil content. It is probable that a higher efficiency would result from sweating at a rate slower than 5 per cent. per hour, especially in the initial stages, when the oil content of the stock is comparatively high.

(6) The effect of viscosity has not been studied in detail, but in the limited experimental work performed on this factor results have been obtained which indicate that oil of higher viscosity is more difficult to remove from the wax, and the resulting wax is therefore of higher oil content.

No experiments were made to ascertain the effect of over-heating in the wax–oil mass, as it is clear from the experiments with oil-free wax that strict control and regulation of the temperature throughout the mass is essential for satisfactory sweating.

References.

[1] Sawyer, Hunter and Nash, *J. Instn Petrol.*, 1940, **26**, 390.
[2] *Idem, ibid.*, 1940, **26**, 430.
[3] *Idem, ibid.*, 1941, **27**, 1.

Department of Oil Engineering and Refining,
University of Birmingham.

OBITUARY.

CARLETON ELLIS.

Carleton Ellis, who was a Fellow of the Institute, died in Miami Beach, Florida, on 13th January last, influenza being the immediate cause of his death. He was born in Keene, New Hampshire, U.S.A., on 20th September, 1876, and received his early training as a chemist at the Massachusetts Institute of Technology, where the degree of Bachelor of Science was conferred upon him in 1900, and where he taught for two years following.

Whilst at this Institute the inventive genius of Carleton Ellis commenced to assert itself, but, as is the experience of most technical men, he early discovered that whilst an original idea might be developed by hard work, patience, and initiative, to turn it to economic value required also hard cash, which went mostly into the pockets of patent agents. He therefore commenced a study of patent law, and in time received a certificate qualifying him to practice before the Patent Office of the United States.

The work of this great industrial scientist was spread over a wide range of organic chemistry, for Carleton Ellis had worked extensively in the field of edible oils, fats, waxes, synthetic resins, paints, varnishes, petroleum products, and gasoline manufacture, and for some years he had governed the Ellis Laboratories at Montclair, New Jersey. In addition to this, he had acted as Consultant on the Technical Committee and Chemical Committee of the Standard Oil Company of New Jersey for a considerable period.

During his career, Carleton Ellis was responsible for more than 700 patents, a record exceeded in the U.S. Patent Office by only two other scientists, Thomas A. Edison and a John O'Connor. The work for which he was best known was in connection with catalytic hydrogenation, petroleum oxidation, chemical derivatives from petroleum, the production of alcohols from still gases, synthetic resins and plastics, and nitrocellulose and analogous derivatives of cellulose.

The results of his researches and studies were presented in the form of such monumental works of reference as : " The Hydrogenation of Organic Substances," " The Chemistry of Synthetic Resins," " The Chemistry of Petroleum Derivatives," " The Chemical Action of Ultra-violet Rays " (considered by a Committee of the League of Nations as one of the most important scientific books of 1925), as well as in numerous papers published in technical journals. As an example of his catholicity, reference might be made to two discoveries for which he was responsible. The first was the finding of a profitable market for the milk recovered from the udders of slaughtered cows. His solution was a dog biscuit made in the shape of a bone, which soon had a ready sale. The other was another of his earlier commercial successes, the development of the Tube and Tank method of cracking heavy petroleum products, which then had a limited use.

Carleton Ellis was a past president of the New Jersey Chemical Society,

a member of the American Chemical Society and of the American Institute of Chemical Engineers, a Fellow of the Chemical Society, and Edward Longstreth medallist of the Franklin Institute. As can be imagined, he was a voracious reader, but, despite his busy life, he found time to devote a certain period every year to travel, in order to meet old friends and, due to his charming personality, he invariably made many new friendships on these occasions.

Some years ago Carleton Ellis spent a short time in the petroleum laboratories at the University of Birmingham, England, when the writer formed a happy and lasting friendship with him : it was soon evident that he possessed the ability of inspiring confidence and the team spirit in his juniors, and of drawing the best from them by his natural pleasing manner and power of leadership.

At the last World Petroleum Congress, members of this Institute had the pleasure of meeting both Carleton Ellis and his charming wife.

To his relatives we extend our deepest sympathy.

A. W. Nash.

JOHN ARTHUR CARPENTER.

John Arthur Carpenter, M.A., F.I.C., a Devonian by birth, was educated at Exeter School. At New College, Oxford, he took First Class Honours in Mathematical "Mods." and Chemical Finals, and later a Second Class in Physics. He was President of the Oxford University Junior Scientific Club, Demonstrator in Chemistry at Christ Church, and Lecturer and Tutor in Physics at University College, Exeter. Subsequently he was a Master in St. Paul's School, London.

He served in the Great War of 1914–18, retiring with the rank of Major.

In 1922 he became Research Chemist in charge of the Experimental Laboratory of the Syriam Refinery of the Burmah Oil Co., Ltd., in which capacity he remained until his sudden death on December 2, 1940.

Carpenter, who became a Member of the Institute in 1925, contributed some useful papers to the *Journal*, including :

"The Physical and Chemical Properties of Paraffin Wax, particularly in the Solid State" (1926, **12**, 288).

"The Composition of Petroleum (Kerosine and other) Fractions, with a Standardization of Miscibility and Optical Tests" (1926, **12**, 518).

(With J. P. Fraser) "Regulation of Velocity of Flow of Fixed Quantities of Liquid over Surfaces" (1927, **13**, 725).

"The Composition of Petroleum (Kerosine and other) Fractions" (1928, **14**, 446).

W. J. Wilson.